

(19) Europäisches Patentamt
 European Patent Office
 Office européen des brevets



(11) Publication number:

0 547 335 A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 92118052.7

(51) Int. Cl.⁵: C03B 37/014, C03B 32/00,
 G02B 6/28

(22) Date of filing: 22.10.92

(30) Priority: 16.12.91 US 809697

(43) Date of publication of application:
 23.06.93 Bulletin 93/25(84) Designated Contracting States:
 DE ES FR GB IT NL(71) Applicant: CORNING INCORPORATED
 Houghton Park
 Corning New York 14831(US)(72) Inventor: Carpenter, Norman Willard, Corning
 Incorporated
 Patent Department, SP FR 02-12
 Corning, NY 14831(US)
 Inventor: Young, Donald Ray, Jr., Corning
 Incorporated
 Patent Department, SP FR 02-12
 Corning, NY 14831(US)
 Inventor: Morrow, Alan John, Corning
 Incorporated
 Patent Department, SP FR 02-12
 Corning, NY 14831(US)(74) Representative: Smith, Sydney et al
 Elkington and Fife, Beacon House, 113
 Kingsway
 London WC2B 6PP (GB)

(54) Method of making fluorine/boron doped silica tubes.

(57) Disclosed is a method of forming a glass tube doped with boron and fluorine. A B_2O_3 -doped tubular porous preform is heated, and a fluorine-containing gas is flowed into its aperture. The temperature is sufficiently high to cause the fluorine-containing gas to decompose and form fluorine which dopes the preform. Also flowed into the aperture is a sufficient amount of BF_3 to prevent fluorine from reacting with the B_2O_3 in the porous preform and forming a B_2O_3 -depleted region near the aperture surface. The particles are then fused to form a fluorine-containing dense glass tube.

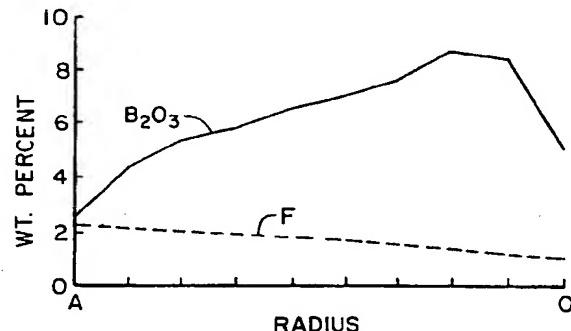


Fig. 1

Background of the Invention

The present invention relates to the manufacture of glass articles having predetermined composition profiles, and more particularly to the manufacture of doped silica tubes having predetermined radial composition profiles of B_2O_3 and fluorine.

Glass tubes having predetermined radial composition profiles are utilized in the manufacture of various optical devices. For example, doped silica tubes having refractive indices lower than that of silica are used in the manufacture of a type of fiber optic coupler referred to as a multilad coupler. Such couplers are formed by inserting into a glass tube at least a portion of each of a plurality of optical fibers so that the fiber portions occupy the midregion of the tube. The tube midregion is collapsed onto fibers, and the central portion of the midregion is stretched until a predetermined coupling occurs between the fibers. Couplers having various kinds of coupling characteristics, e.g. WDM, (wave division multiplexing), achromatic, and the like, have been made by this process. See for example, U.S. patents 4,931,076 and 5,011,251.

The physical characteristics of the glass tube affect both the manufacturing process and the optical characteristics of the resultant coupler. Such physical characteristics include viscosity, refractive index and thermal coefficient of expansion (TCE).

In multilad fiber optic couplers, the tube refractive index n_3 must be lower than the refractive index n_2 of the fiber cladding. Commercially available single-mode optical fibers usually have a value of n_2 that is equal to or near that of silica. If silica is employed as the base glass for the tube, a dopant is added thereto for the purpose of decreasing n_3 to a value lower than n_2 . The refractive index of the tube relative to that of the cladding is represented by Δ_{2-3} , the value of which is defined as

$$\Delta_{2-3} = (n_2^2 - n_3^2)/2n_2^2$$

The value of Δ_{2-3} for standard WDM couplers has usually been between 0.26% and 0.35%. During the manufacture of achromatic overclad couplers, process reproducibility is enhanced by employing preforms having Δ_{2-3} values above 0.35%. When employed in the manufacture of fiber optic couplers, the refractive index of that half of the tube having the smaller radius is more critical since it is adjacent to the optical fibers and therefore propagates the coupled signal in the coupling region.

The dopants B_2O_3 and fluorine have been employed to lower the refractive index of silica tubes, fluorine having the greater effect on refractive index. They also advantageously decrease the tube viscosity to a value lower than that of the coupler

fibers, boron having the greater effect on viscosity. This enhances to a certain extent the collapsing of the tube onto the fibers; the tube glass flows around the fibers without distorting their shape. These dopants also affect the TCE of the tube, boron increasing the TCE relative to silica, while fluorine reduces the TCE relative to silica when used in concentrations needed for couplers. The TCE of the tube can affect the polarization sensitivity of the resultant coupler. The TCE of the tube is usually tailored to be compatible with that of the fiber cladding. For a specific coupler, the concentration of boron and fluorine in the glass tube are selected to provide the optimal combination of the above-discussed optical and mechanical characteristics.

Glass coupler tubes have been made by a flame oxidation process involving the following steps: (1) deposition of glass particles on a mandrel, (2) mandrel removal, and (3) consolidation of the resultant porous preform. That process has been used to make coupler tubes comprising SiO_2 doped with 1 to 12 wt. % B_2O_3 , SiO_2 doped with 0.1 to approximately 2.5 wt. % fluorine, and SiO_2 doped with combinations of B_2O_3 and fluorine. To achieve the desired combination of physical properties needed for a particular coupler, a combination of both dopants is usually needed. The boron has conventionally been added to the glass particle stream during the particle deposition step. However, when the required amount of fluorine exceeds about 0.6 wt. % (0.2% Δ), the fluorine cannot be incorporated into the preform during the particle deposition step since fluorine in the reactant vapor stream reacts with water in the air to form HF. Also, it has been found that the addition of a fluorine-containing compound to the reactant stream emitted by a flame hydrolysis burner tends to decrease the rate of deposition of glass particles collected on the mandrel. Fluorine has therefore been added to the glass during the consolidation step.

The standard process for producing coupler tubes containing both boron and fluorine is as follows. A porous preform having a uniform radial composition of B_2O_3 -doped SiO_2 is formed on a mandrel by a process such as that disclosed in U.S. Pat. No. 4,165,223 and patents cited therein. The reactants, $SiCl_4$ and BCl_3 are supplied to a flame hydrolysis burner that directs a stream of B_2O_3 -doped SiO_2 particles toward the mandrel. After a coating of sufficient thickness is built up, the mandrel is removed, and the resultant tubular porous preform is placed in a consolidation furnace. The preform is then doped with fluorine by flowing into the preform aperture a mixture of He and a source of fluorine such as SiF_4 , CF_4 or the like. These fluorine-containing reactants are less corrosive than fluorine gas, and they effectively

dissociate to active fluorine in the consolidation furnace. The radial composition profiles of the resultant tubes are typically as illustrated in Fig. 1. The low concentrations of B_2O_3 near the tube aperture is the result of the reaction of the B_2O_3 in the porous preform with F in the gas mixture to form BF_3 which volatilises and is exhausted from the furnace. This composition profile demonstrates the poor stability of the tube making process. Reproducibility of the process of manufacturing overclad couplers depends upon the uniformity of the radial composition profile of the overclad tube.

Attempts have been made to dope a pure silica porous preform with both boron and fluorine by flowing BF_3 into the preform aperture while the preform is heated in a consolidation furnace. The resultant radial composition profile is shown in Fig. 2. While the radial concentration of fluorine is relatively uniform, the radial concentration of B_2O_3 is unacceptable since it is much higher at small tube radii than at large tube radii.

Summary of the Invention

It is therefore an object of the present invention to provide a method of making glass tubes containing B_2O_3 and fluorine. Another object is to provide a reproducible method of making such tubes so that particular radial composition profiles of B_2O_3 and fluorine are consistently achieved.

Briefly, the present invention relates to a method of forming a glass article. A B_2O_3 -doped porous glass preform is initially formed. The preform is heated, and a fluorine-containing gas is flowed through its pores to dope it with fluorine. The porous preform is then consolidated to form a dense glass article doped with fluorine and B_2O_3 . The method of the invention is characterized in that the step of flowing includes flowing through the preform pores a sufficient amount of BF_3 to inhibit the reaction of fluorine with B_2O_3 in the porous preform, since that reaction tends to form a B_2O_3 -depleted region.

The porous preform preferably has an aperture, and the fluorine-containing gas is flowed between the aperture and the outer surface of the preform. In that embodiment wherein the fluorine-containing gas flows into the aperture, at least a portion of the gas flows through the pores to the outer surface whereby the reaction products can be flushed away by a muffle gas. The aperture-containing preform can be formed by depositing layers of B_2O_3 -doped SiO_2 particles on the surface of a mandrel and removing the mandrel from the preform to form the aperture. Additional dopants such as germania can be incorporated in the glass particles to modify certain physical characteristics of the resultant preform.

When used as a tube for making overclad fiber optic couplers, that half of the dense glass tube having the smaller radius must have substantially uniform radial composition profiles of B_2O_3 and fluorine. Such tubes can be reproducibly formed by the present method. Indeed, the method of this invention routinely results in the formation of dense glass tubes having substantially uniform composition profiles of B_2O_3 and fluorine throughout the entire tube radius.

Brief Description of the Drawings

Figs. 1 and 2 are graphs illustrating radial variations in tube composition profile when conventional tube making methods are employed. In these figures, A and O represent the radii of the aperture and the outer surface, respectively.

Fig. 3 illustrates the application of a coating of glass particles to a mandrel.

Fig. 4 is a schematic representation of a consolidation furnace.

Fig. 5 is a graph illustrating the tube radial composition profile when the present method is used.

Description of the Preferred Embodiments

The present method pertains to a multistep doping process that results in the formation of a glass tube having desired boron and fluorine concentration profiles. Initially formed is a porous glass preform having a predetermined B_2O_3 concentration profile. While it is at an elevated temperature, the porous preform is subjected to a gas mixture containing a first source of fluorine for doping the preform and a sufficient amount of BF_3 to inhibit the reaction of fluorine in the gas stream with boron in the preform to form BF_3 , a reaction that would result in the depletion of boron from the porous preform. For example, BF_3 can be supplied to the porous preform along with conventional fluorine compounds such as SiF_4 , CF_4 or the like. Fluorine gas could be used, but it is very difficult to handle.

After the preform is doped with fluorine, it is heat treated to fuse or consolidate it into a non-porous glassy body. This step can be performed in a furnace separate from that in which the fluorine doping step occurred, but the fluorine doping and consolidation steps are preferably performed in a single furnace, complete consolidation occurring after the doping step. Suitable consolidation furnaces are disclosed in U.S. Patents Nos. 4,165,223 and 4,741,748. The scanning consolidation furnace disclosed in U.S. Patent No. 4,741,748 is advantageous in that one source of heat in the preform is generated by a coil that scans along the preform. A sharp hot zone can be generated by slowly travers-

ing the coil along the preform; alternatively, the preform can be isothermally heated by rapidly reciprocating the coil. Moreover, the temperature of a scanning consolidation furnace is readily adjustable.

The preform preferably contains an aperture for the purpose of facilitating the flow of fluorine-containing gases through its pores. A tubular porous preform is conventionally formed by depositing particles on a mandrel and then removing the mandrel. The particle deposition step can take the form of any process whereby heated glass particles are deposited to form an aggregation or deposit of particles that adhere together to form a tubular, porous glass coating having interconnective pores.

A suitable process for forming a boron-doped tubular porous preform is shown in Fig. 3 wherein the large diameter end of a tapered mandrel 10 extends through a glass tube 11 having protrusions 12. Mandrel 10 is rotated and translated with respect to a burner 13 which may be of the type disclosed in U.S. Patent 4,165,223. Reactant compounds emanate from the burner where they are oxidized in the flame to form glass particle stream 22 which is directed toward mandrel 10. Auxiliary burners 23 direct flames toward the ends of the porous glass preform during deposition; the use of auxiliary burners is taught in U.S. Patent 4,810,276 (Gilliland). A porous preform 28 of desired thickness is formed by traversing the mandrel a number of times with respect to burner 13 to cause a build-up of a plurality of layers of glass particles.

Preform 28 is removed from the lathe, and the mandrel is removed through tube 11, thereby leaving a longitudinal aperture 31 in the porous preform. Protrusions 12 cause tube 11 to adhere to the preform; that tube supports the preform during subsequent processing.

Fig. 4 shows the resultant tubular porous preform 28 suspended in the muffle 35 of a consolidation furnace where it is dried, doped and consolidated. Muffle gas represented by arrows 36 are fed to the bottom of muffle 35. Flowed through tube 11 and into aperture 31 is a gas mixture (arrows 37) comprising an inert gas such as helium and a source of an amount of fluorine sufficient to dope the preform. As described above, gas mixture 37 also contains an amount of BF_3 sufficient to prevent the B_2O_3 depletion shown in Fig. 1. Therefore, the radial B_2O_3 concentration remains quite uniform as shown in Fig. 5. The concentration profiles of Fig. 5 result from treating a porous B_2O_3 -doped silica preform with BF_3 and SiF_4 at an elevated temperature.

The concentration of B_2O_3 and fluorine in the resultant glass tube are determined by controlling the amount of B_2O_3 deposited during the particle deposition step and by controlling the concentra-

tion and flow rate of fluorine-containing gas used in the doping step. Other factors that affect the concentrations of each of these dopants are preform density, time and temperature of the doping step, and the flow rate of other gases such as oxygen in the dopant gas stream.

For certain reasons, such as modification of viscosity and/or TCE without changing refractive index, it may be desirable to add another dopant such as germania to the glass particles during the formation of preform 28. For example, a porous $\text{SiO}_2\text{-B}_2\text{O}_3\text{-GeO}_2$ preform could be formed on a mandrel as described above, GeCl_4 being fed to the burner along with SiCl_4 and BCl_3 .

The following specific example illustrates the manner in which the method of the present invention can be employed to produce doped silica tubes having substantially uniform radial composition profiles of B_2O_3 and fluorine. The term "substantially uniform" is used herein to mean that the radial concentration of a dopant does not vary from an average value by more than 0.5 wt. percent.

Alumina mandrel 10 (Fig. 3) was inserted into glass tube 11. The outside diameter of the mandrel tapered from 9.5 mm to 12.6 mm over its 107 cm length. The ends of mandrel 10 were mounted in a lathe where it was rotated and translated with respect to burner 13, which was positioned 17.2 cm from mandrel 10. Auxiliary burners 23 directed flames toward the ends of the porous glass preform during deposition. The burner traversed a 70 cm section of the mandrel in 30 seconds. An acetylene torch was initially supported on the burner, and the torch traversed the mandrel three times to deposit carbon particles on it to facilitate removal of the porous preform from the mandrel. Thereafter, layers of silica particles doped with B_2O_3 were redeposited by flowing SiCl_4 and BCl_3 to burner 13 in accordance with the following program for 650 traverses of the burner with respect to the mandrel. The flow rate of SiCl_4 remained constant at 1.75 slpm during the first 100 burner traverses; it then linearly decreased from 1.75 slpm to 1.0 slpm from the 101st to the 650th traverse. The flow BCl_3 remained constant at 160 sccm for the first 200 traverses of the burner with respect to the mandrel; it then linearly increased from 160 sccm to 200 sccm from the 201st to the 650th traverse. The term "slpm" means standard liters per minute, and the term "sccm" means standard cubic centimeters per minute. The reactant vapors were premixed with oxygen before being supplied to burner 13. Particle deposition continued for 325 minutes; the preform was then cooled, and the mandrel was removed through tube 11. The resultant porous preform 28 was 75 cm long, 90 mm in diameter, and its average density was about 0.35

g./cm³.

Preform 28 was then loaded into a scanning consolidation furnace (Fig. 4) where it was dried, doped and consolidated. During each of these steps, a muffle gas consisting of 20 slpm helium flowed upwardly from the bottom of the muffle.

During the drying step, a movable induction coil was reciprocated back and forth along the length of the preform at a rate of 1800 mm/minute to isothermally increase its temperature from room temperature to about 1025°C. A drying gas mixture consisting of 500 sccm oxygen, 70 sccm chlorine and 700 sccm helium flowed through tube 11 and into the axial aperture from which the mandrel had been removed. While the temperature remained at 1025°C, this gas mixture continued to flow for 20 minutes to dry the preform.

During the subsequent preform doping step, the induction coil continued to reciprocate at 1800 mm/minute to maintain the preform temperature at 1025°C. During this step, the duration of which was 20 minutes, a doping gas mixture consisting of 500 sccm oxygen, 70 sccm chlorine, 700 sccm helium, 50 sccm BF₃ and 200 sccm SiF₄ flowed into the axial aperture. The SiF₄ decomposed to form fluorine which diffused into and doped the B₂O₃-SiO₂ particles. The presence of BF₃ in the preform interstices prevented the depletion of B₂O₃ from the preform.

The porous preform was then consolidated to form a dense glass tube by traversing the coil upwardly along the preform at a rate of 12 mm/minute to generate in the preform a sharp hot zone, the maximum temperature of which was about 1440°C. The drying gas mixture continued to flow during the entire consolidation step.

Since the B₂O₃ was not depleted from the porous preform during the doping step, the resultant tube exhibited the composition profile shown in Fig. 5. The tube was stretched to decrease its diameter, and it was severed into individual capillary tubes, each having a length of 3.4 cm, a 2.65 mm outside diameter and a 270 µm longitudinal aperture diameter. Both ends of the aperture were flared outwardly by the method taught in European published application 0423999 (G.E. Berkey 19).

The aforementioned tubes were employed to make 1x2 fiber optic couplers in accordance with the method disclosed in U.S. patent No. 4,979,972, which is incorporated herein by reference. In accordance with that method, approximately 3.2 cm of coating is stripped from the central region of a 3 meter length of 125 µm diameter single-mode optical fiber (the first fiber) having a 250 µm diameter urethane acrylate coating. This fiber is threaded through the capillary tube until the stripped region is located just below the tube. A 6 cm long section of coating is removed from the end of a 1.5 meter

length of a second fiber. The second fiber is severed, and its end is rounded in a flame, the uncoated length of fiber being about 2.9 cm. Both fibers are inserted into the capillary tube until the uncoated regions are centered in the aperture. The tube is evacuated, and its midregion is heated to collapse it onto the fibers. The center portion of the midregion of the resultant structure is stretched to provide the desired coupling ratio. After the coupler has cooled, a drop of adhesive is applied to each end of the capillary tube.

When an input signal is propagated in the first fiber at one end of the coupler, the resultant device couples approximately 50% of the signal to each of the two optical fibers extending from the opposite end.

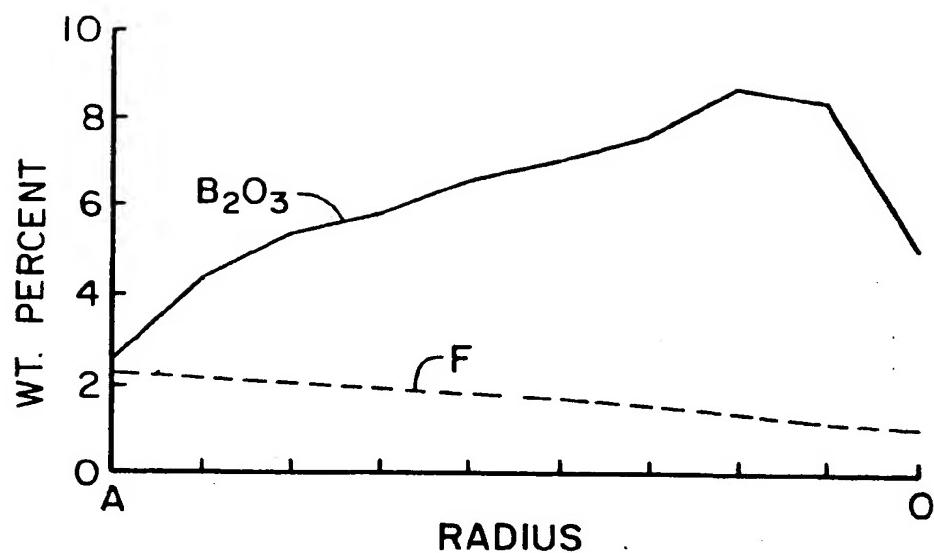
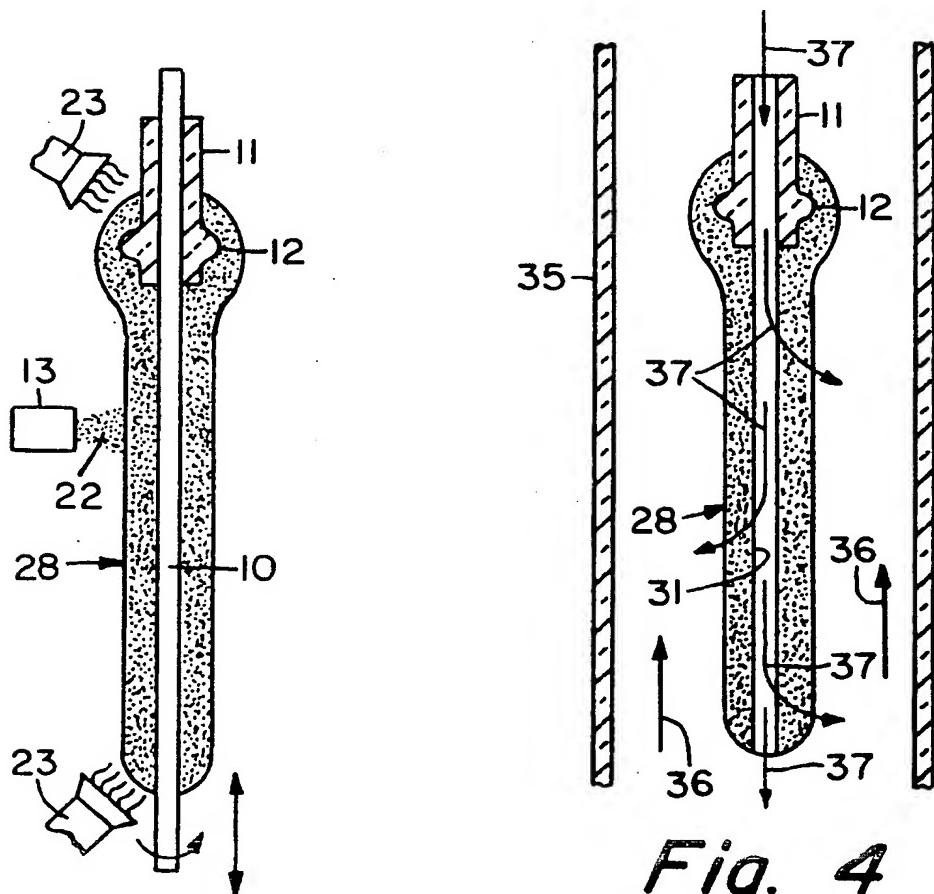
This process typically produced 3 dB couplers that operated at 1310 nm. After the process was tuned, the couplers which were made thereby exhibited a median excess device loss was about 0.15 dB, and a median coupling ratio of 50.8. The lowest measured loss was 0.02 dB.

The use of the uniform composition tubes improved the reproducibility of the process of making fiber optic couplers. For example, the standard deviation of the coupling ratio was about 13% when the process employed tubes having composition gradients of the type shown in Fig. 1. The standard deviation of the coupling ratio decreased to about 5.5% when the process employed tubes having composition ratios of the type shown in Fig. 5.

Claims

- 35 1. A method of forming a glass article comprising
the steps of
forming a B₂O₃-doped porous glass
preform having interconnective pores,
heating said preform,
doping said heated preform with fluorine,
and
consolidating said porous preform to form
a dense glass article doped with fluorine and
B₂O₃, characterized in that the step of doping
includes flowing through said pores an agent
that inhibits the depletion of boron from
preform.
2. Method according to claim 1, wherein the step
of doping comprises flowing through said
pores a fluorine-containing gas which includes
flowing through said pores a sufficient amount
of BF₃ to prevent fluorine from reacting with
the B₂O₃ in said porous preform and forming a
B₂O₃-depleted region therein.
3. Method according to claims 1 or 2, wherein the
step of forming comprises depositing on a

- cylindrical mandrel a coating of glass particles comprising SiO₂ and B₂O₃, said coating containing interconnective pores,
 removing said mandrel to form a porous glass preform having an axial aperture,
 inserting said preform into a consolidation furnace muffle,
 flowing upwardly through said muffle a muffle gas comprising an inert gas,
 flowing a fluorine-containing gas mixture into said aperture, at least a portion of said gas mixture flowing outwardly through said pores, said gas mixture comprising (a) a first, boron-free fluorine compound that decomposes to form fluorine which dopes said preform, and (b) a sufficient amount of BF₃ to prevent fluorine from reacting with the B₂O₃ in said porous preform and forming a B₂O₃-depleted region near the aperture surface, and
 heating said preform to a temperature within the consolidation temperature range for a time sufficient to cause said particles to fuse and form a dense glass tube.
4. Method in accordance with claim 1, 2 or 3 wherein the step of forming comprises forming a tubular glass article having an aperture, and the step of flowing comprises flowing fluorine-containing gas between said aperture and the outer surface of said preform.
5. Method in accordance with claim 4 wherein the step of flowing comprises flowing fluorine-containing gas into said aperture, at least a portion of said gas flowing through said pores to the outer surface of said preform.
6. Method in accordance with any one of claims 1-5, wherein the step of forming comprises depositing layers of particles doped with B₂O₃, or with B₂O₃ and GeO₂ or another dopant on the surface of a mandrel to form a porous preform and removing said mandrel from said preform to form said aperture.
7. A method in accordance with claim 6 wherein the step of consolidating results in the formation of a dense glass tube, the entire tube or that half having the smaller radius having substantially uniform radial composition profiles of B₂O₃ and fluorine.
8. Method in accordance with any one of claims 1-7, wherein the step of doping comprises subjecting said heated porous preform to a gas including a fluorine compound and BF₃.
9. Method in accordance with claim 8 wherein the step of consolidating results in the formation of a dense glass tube in which that half having the smaller radius has substantially uniform radial composition profiles of B₂O₃ and fluorine, or in the formation of a dense glass tube having substantially uniform radial composition profiles of B₂O₃ and fluorine.
10. Method of forming a fiber optic coupler comprising depositing on a cylindrical mandrel a coating of glass particles comprising SiO₂ and B₂O₃, said coating containing interconnective pores,
 removing said mandrel to form a porous glass preform having an axial aperture,
 inserting said preform into a consolidation furnace muffle,
 flowing a fluorine-containing gas mixture into said aperture, at least a portion of said gas mixture flowing outwardly through said pores, said gas mixture comprising (a) a boron-free fluorine compound that decomposes to form fluorine which dopes said preform, and (b) BF₃,
 heating said preform to a temperature within the consolidation temperature range for a time sufficient to cause said particles to fuse and form a dense glass tube having first and second opposite end portions and a midregion, a longitudinal aperture extending from a first end of said tube to a second end thereof,
 disposing a plurality of optical fibers such that at least a part of each fiber extends into the longitudinal aperture of said glass tube, each of said fibers having a core and cladding, at least that part of each fiber that is located in said tube midregion having no coating thereon, each of said fibers extending beyond at least one end of said tube,
 collapsing said tube midregion onto said fibers, and stretching the central portion of said midregion.

*Fig. 1**Fig. 3**Fig. 4*

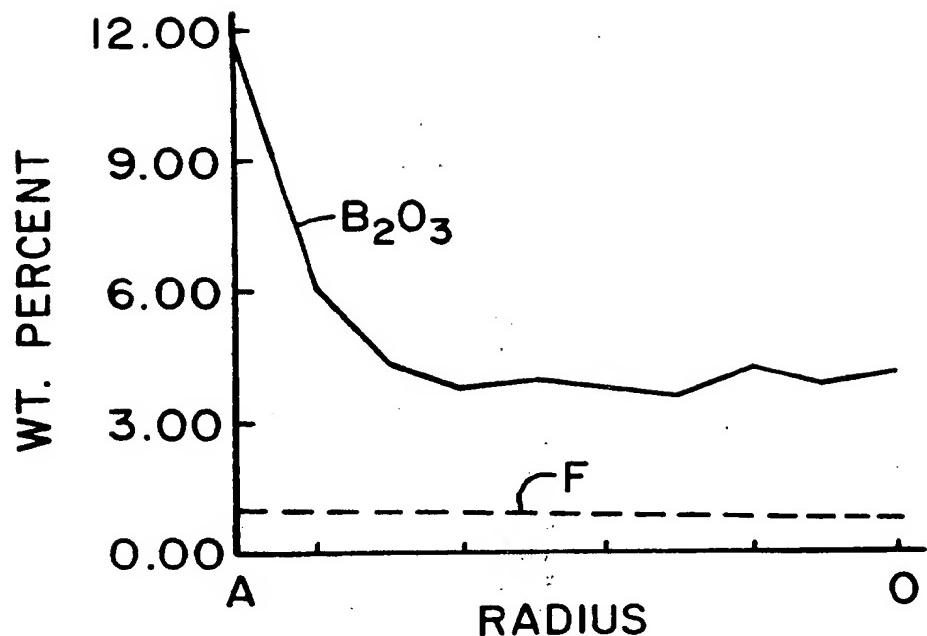


Fig. 2

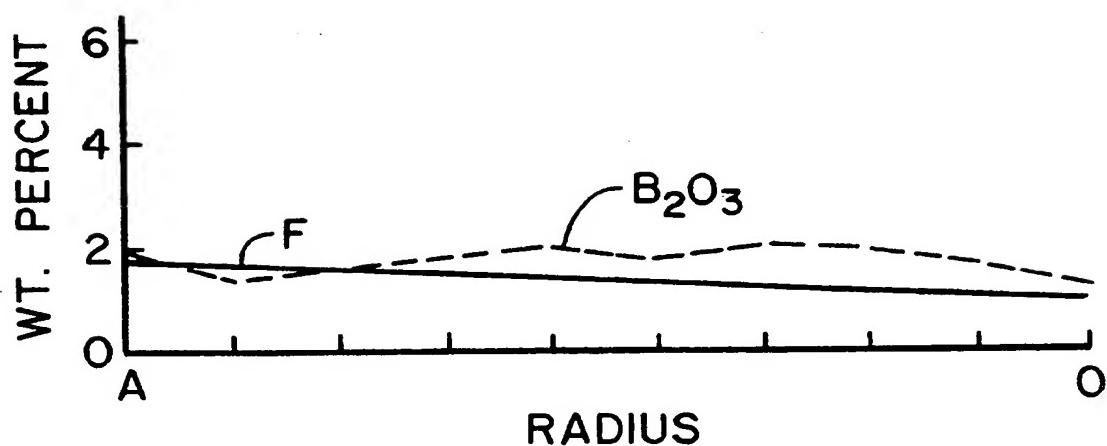
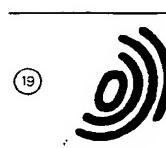


Fig. 5



(19) Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 547 335 A3

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 92118052.7

(51) Int. Cl.⁵: **C03B 37/014, C03B 32/00,
G02B 6/28**

(22) Date of filing: **22.10.92**

(30) Priority: **16.12.91 US 809697**

(71) Applicant: **CORNING INCORPORATED
Houghton Park
Corning New York 14831(US)**

(43) Date of publication of application:
23.06.93 Bulletin 93/25

(72) Inventor: **Carpenter, Norman Willard, Corning
Incorporated
Patent Department, SP FR 02-12
Corning, NY 14831(US)**
Inventor: **Young, Donald Ray, Jr., Corning
Incorporated
Patent Department, SP FR 02-12
Corning, NY 14831(US)**
Inventor: **Morrow, Alan John, Corning
Incorporated
Patent Department, SP FR 02-12
Corning, NY 14831(US)**

(84) Designated Contracting States:
DE ES FR GB IT NL

(74) Representative: **Smith, Sydney et al
Elkington and Fife, Beacon House, 113
Kingsway
London WC2B 6PP (GB)**

(88) Date of deferred publication of the search report:
25.08.93 Bulletin 93/34

(54) Method of making fluorine/boron doped silica tubes.

(57) A B_2O_3 -doped tubular porous silica preform is heated, and a fluorine-containing gas, such as SiF_4 or CF_4 , is flowed into its aperture. The temperature is sufficiently high to cause the fluorine-containing gas to decompose and form fluorine which dopes the preform. Also flowed into the aperture is a sufficient amount of BF_3 to prevent fluorine from reacting with the B_2O_3 in the porous preform and thereby inhibit formation of a B_2O_3 -depleted region near the aperture surface.

The doped porous preform is then consolidated to fuse the particles and form a dense glass tube containing both boron and fluorine as dopants with substantially uniform radial composition profiles (see fig.5). Optical fibres can be placed in the dense glass tube which is then collapsed to form a fibre optic coupler.

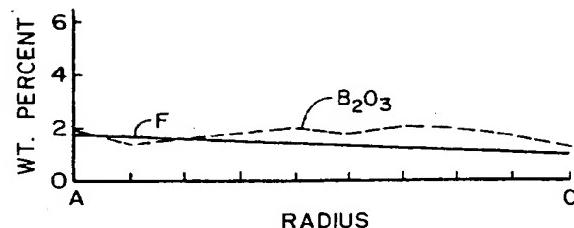


Fig. 5



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 11 8052
Page 1

DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)						
P, X	PATENT ABSTRACTS OF JAPAN vol. 16, no. 249 (C-948)8 June 1992 & JP-A-04 055 333 (FURUKAWA ELECTRIC CO.LTD.) 24 February 1992 * abstract and lower left-hand columns on second and third pages * ---	1, 2, 8	C03B37/014 C03B32/00 G02B6/28						
P, X	PATENT ABSTRACTS OF JAPAN vol. 16, no. 518 (C-999)26 October 1992 & JP-A-04 193 727 (FURUKAWA ELECTRIC CO.LTD.) 13 July 1992 * abstract; column 6; figure 1 * * column 4; figure 1 * ---	1, 2, 8							
X	PATENT ABSTRACTS OF JAPAN vol. 10, no. 98 (C-339)15 April 1986 * abstract *	1							
Y	& CHEMICAL ABSTRACTS, vol. 104, no. 24 Columbus, Ohio, US; abstract no. 211858q, * abstract * & DATABASE WPIL Section Ch, Week 01, Derwent Publications Ltd., London, GB; Class L01, AN 86-004190 * abstract * & JP-A-60 231 435 (SHOWA ELECTRIC WIRE CO.LTD.) 18 November 1985 ---	2-10							
Y	PATENT ABSTRACTS OF JAPAN vol. 11, no. 349 (C-456)14 November 1987 & JP-A-62 123 037 (FURUKAWA ELECTRIC CO.LTD.) * abstract *	2, 3, 8, 10 -/-	C03B C03C						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>04 JUNE 1993</td> <td>STROUD J.G.</td> </tr> </table> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>				Place of search	Date of completion of the search	Examiner	THE HAGUE	04 JUNE 1993	STROUD J.G.
Place of search	Date of completion of the search	Examiner							
THE HAGUE	04 JUNE 1993	STROUD J.G.							



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 11 8052
Page 2

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 222 501 (CORNING GLASS WORKS) * claims 1-5; column 4, line 32 to column 5, line 14; column 7, lines 16-38; example 1 ---	3-7, 9, 10	
Y,D	US-A-5 011 251 (W.J.MILLER ET AL.) ---	10	
A	DATABASE WPIL Section Ch, Week 29, Derwent Publications Ltd., London, GB; Class L01, AN 88-201692 & JP-A-63 139 026 (FURUKAWA ELECTRIC CO.LTD.) 10 June 1986 * abstract *---	1-3, 8, 10	
A	DATABASE WPIL Section Ch, Week 43, Derwent Publications Ltd., London, GB; Class L01, AN 85-267364 & JP-A-60 180 928 (FURUKAWA ELECTRIC CO.LTD.) 14 September 1985 * abstract *---	1-3, 7, 9, 10	
A	DATABASE WPIL Section Ch, Week 15, Derwent Publications Ltd., London, GB; Class L01, AN 86-098549 & JP-A-61 044 725 (FURUKAWA ELECTRIC CO.LTD. ET AL.) 4 March 1986 * abstract *---	1-3, 8, 10	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	PATENT ABSTRACTS OF JAPAN vol. 11, no. 290 (C-447)18 September 1987 & JP-A-62 083 323 (SUMITOMO ELECTRIC IND.LTD.) 16 April 1987 * abstract *---	1-3, 8, 10	
A,D	US-A-4 931 076 (G.E.BERKEY) -----	10	
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	04 JUNE 1993	STROUD J.G.	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

